

# PATENT SPECIFICATION

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## (54) IMPROVEMENTS IN OR RELATING TO THE PREPARATION OF ALUMINIUM ALLOYS FOR FINISHING

(71) We, SHIPLEY COMPANY, INC., a Corporation organised and existing under the laws of the Commonwealth of Massachusetts, of 2300 Washington Street, Newton, Massachusetts, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process and compositions for preparing aluminum alloys containing at least 0.1 per cent silicon for finishing and has for its principal object, the treatment of an aluminum alloy surface to form a coating of aluminum substantially enriched in silicon and other alloying metals that is resistant to oxidation and receptive to coating.

The decoration and protection of aluminum and its alloys by the application of coatings, particularly metal coatings, results in aluminum parts having highly desirable properties. The prior art has experienced considerable difficulty in its attempts to deposit adherent coatings on aluminum because of the position of aluminum in the electrochemical series together with the high affinity of the metal for oxygen. The persistence of a tenacious oxide film present on the surface of aluminum prevents adequate adhesion between substrate and coating. Removal of the oxide, followed by short exposure to the atmosphere or an aqueous environment results in the rapid formation of a fresh oxide film. Consequently, it has been found necessary in the prior art to metal plate over aluminum immediately following removal of the oxide film.

Numerous attempts have been made to increase adhesion between an aluminum substrate and its coating and to overcome the

above-noted difficulties. One procedure, known as the zincate process, involves the application of a zinc undercoating to an aluminum surface prior to coating with a desired surface metal. This procedure is cumbersome and requires some 12 to 21 process steps. Because of its position in the electrochemical series, the zinc coating aggravates the corrosion of aluminum and aluminum alloys during use of the plated material. Upon exposure to elevated temperatures, zinc diffuses into aluminum resulting in a loss of bond between the aluminum substrate and a subsequently applied metal coating.

Chemical etching of aluminum and its alloys to remove oxide films followed immediately by deposition of a thin coating of metal by immersion in a metallic salt solution is an additional method previously used to deposit metal coatings on aluminum. The etching step involves immersion of the aluminum part in a chemical etchant such as caustic soda, caustic soda plus sodium chloride, hydrochloric acid plus nitric acid, hydrofluoric acid, hydrofluoric acid plus nitric acid, etc., for a brief period of time sufficient only to dissolve the oxide coating. Conditions are critical. Should the aluminum part be over-etched, the prior art has found it necessary to treat the part with nitric acid or a mixture of nitric and hydrofluoric acid to remove all surface layers formed during the etching step to thereby provide a bright, shiny surface for metal plating. This surface must immediately be plated or maintained in a non-oxidising atmosphere to prevent formation of fresh oxide film.

A similar process involves an etch solution containing heavy metallic salts such as salts of copper, nickel, or manganese to give an immersion deposit of metal during the etching process. The deposit acts as a base upon which

[Price 25p]

a desired metal may be deposited. At the present time, the process has not been found to give satisfactory coatings.

The present invention provides a facile procedure for preparing aluminum alloys containing at least 0.1 per cent silicon for subsequent metal plating. The invention is predicated upon the discovery that a visible, adherent coating, resistant to oxidation and receptive to finishing operations is formed on the surface of an aluminum alloy part by treatment in a halide composition, to be described hereinafter, for a time in excess of that required to remove any oxide coating on the surface of the alloy and sufficient to selectively dissolve aluminum from the oxide-free surface of the alloy leaving silicon and other insoluble alloying ingredients behind as a coating. This coating, hereinafter referred to as a "conversion coating", is composed of aluminum substantially enriched in silicon and other alloying constituents. Because the conversion coating is oxidation resistant, an aluminum part may be prepared in accordance with the invention, and thereafter stored or transported in air without formation of a damaging oxide film that would act to prevent adhesion between a metal coating and the aluminum substrate. Metal plated directly over the conversion coating is extremely adherent to the aluminum substrate and possesses good surface appearance.

In order to obtain the benefits of oxidation resistance, adhesion and appearance, the conversion coating must be characterized by uniform displacement over the entire surface of the aluminum part to be plated. The conversion coating normally appears on the aluminum as a visible, white to dark grey layer, dependent upon alloying constituents.

The conversion coating is formed by immersion of the aluminum part in a solution capable of selectively dissolving aluminum from the surface of the part leaving silicon and other alloying elements less soluble than silicon in the solution behind as a uniform and adherent coating. This solution, hereinafter referred to as the "activator solution" has a composition as follows:

(a) Halide ion other than the fluoride ion. The halide ion can be derived from an acid such as hydrochloric acid, hydrobromic acid, hydroiodic acid, and mixtures thereof, or from metal salts of these acids where the metal cation does not deposit on the aluminum substrate. Examples of suitable salts include beryllium chloride, ammonium chloride, aluminum bromide and the alkali and alkaline earth metal halides other than fluorides such as sodium chloride, sodium bromide, sodium iodide, potassium chloride, potassium bromide, magnesium chloride, calcium bromide, calcium iodide, lithium chloride, magnesium bromide, etc.

(b) Solvent that may be water or a mixture of water and an inert organic solvent soluble

in water and non-reactive with solution components. Typical organic solvents include, by way of example, formamide; alcohols such as methyl alcohols, propyl alcohol, butyl alcohol; glycols such as ethylene glycol, butylene glycol, mesitylene glycol, propylene glycol; ethers of ethylene glycol—i.e. the cellosolves such as butyl cellosolve, methyl cellosolve, phenyl cellosolve; ketones such as acetone, acetophenone, butanone.

(c-1) Hydrogen ion that may be derived from an acid other than hydrofluoric acid such as hydrochloric acid, sulfuric acid, citric acid, phosphoric acid, hydrobromic acid, hydrolic acid, acetic acid, sulfonic acid and mixtures thereof; and/or

(c-2) An oxidizing agent such as the ferric ion, the ceric ion, permanganate, peroxide, chromate.

In addition to the above, organic inhibitors for aluminum may be added to the formulation to control the rate of dissolution and minimize smut formation. Materials of this nature are well known in the art and are described in numerous publications including Hudson and Warning, Metal Finishing, October, 1966, pp. 58 to 63, incorporated herein by reference. Typical examples of these materials include nonheterocyclic compounds of nitrogen such as n-dodecylamine, tridodecylamine, aniline, cyclohexylamine, p-toluidine, alpha-naphthylamine, etc; heterocyclic compounds of nitrogen such as pyrrole, pyrrolidine, indole, indoline, carbazole, pyridine, 4-picoline, quinoline, quinaldine, 2,6-dimethylquinoline, pyrimidine, pyrazine, piperazine, melamine, hexamethylenetetramine, urea; organic sulfur compounds such as thiourea, thiophene, benzothiophene, thiazole, benzothiazole, s-trithiane; organic compounds free of sulfur or nitrogen such as formaldehyde, benzaldehyde, 2-butyn-1,4-diol, chlorendic acid, methyl butynol, pentachlorophenol, resorcinol, catechol, hydroquinone, and mixtures thereof. Of the above, formaldehyde, urea, thiourea, methyl butynol, chlorendic acid, pentachlorophenol, resorcinol, catechol, and hydroquinone are preferred.

In the above formulations, the halogen ion and hydrogen ion may be derived from the same acid such as hydrochloric acid or the hydrogen ion concentration may be increased by a combination of acids such as hydrochloric acid and sulfuric acid. The inhibitor and the organic solvent act to control the rate of the aluminum dissolution, and in some cases, minimize smut formation. It should be understood that three classes of activator solutions are contemplated;—i.e. one containing hydrogen ions, one containing an oxidizing agent, and one containing a combination of hydrogen ions and an oxidizing agent.

The above compositions are formulated to selectively etch aluminum in preference to silicon to form a conversion coating. This coating, on its surface is substantially all silicon and alloying elements that dissolve in

the activator solution at a slower rate than aluminum. With increasing depth of the conversion coating, the aluminum concentration increases until the composition of the original alloy is reached. The total depth of the conversion coating is usually less than one mil.

The concentration limits for the constituents of the activator solution may vary within very broad ranges dependent upon treatment temperature, aluminum alloy composition, the constituents of the activator solution and its ability to etch aluminum ratio of volume of activator solution to size of part treated. In general, the activator solution should be formulated to provide a relatively slow rate of aluminum dissolution. The time to dissolve the aluminum from the surface of the part to be plated and form the above-described conversion coating should exceed at least 15 seconds, and preferably two minutes. If the etching rate is too rapid, gas evolution at the surface of the aluminum part possibly causes fracture of the conversion coating and formation of a non-adherent smut. In addition, it is believed that as the oxide film dissolves and the etching of aluminum proceeds, a greater surface area of bare aluminum metal is exposed and heat is generated. This causes a greatly increased rate of reaction resulting in loss of control and undercutting of the conversion coating with additional formation of non-adherent smut.

The following table illustrates preferred concentration limits for the activator solution:

Material	Concentration
Halide ion (moles/liter)	0.1 to 6.0
Inhibitor (gms/liter)	1 to 75
Hydrogen ion (moles/liter)	1 to 4
Oxidant (moles/liter)	0.3 to 1.5
Solvent	to 1 liter

The solvent in the above formulations may be water or a mixture of water and the above-identified organic solvents. The total water content may be supplied by an aqueous solution of an acid; the remainder being organic solvent. It should be understood that the above concentration limits are preferred and may be varied considerably, provided the time to etch aluminum and form the conversion coating exceeds 15 seconds.

Though the halide ion of the activator solution may not be fluoride, small quantities of fluoride impurity in the halide may be tolerated provided it is not present in sufficient quantity to damage the conversion coating.

The activator solutions may be used at temperatures ranging between room temperature and the boiling point of the solution dependent upon solution strength. Temperatures below 120°F are preferred as lower temperatures favor slower rates of reaction.

The time of immersion in the activator solution is critical. If the time of immersion

is inadequate, the conversion coating will not form on the aluminum part or will not be uniformly displaced over its entire surface. This results in poor adhesion between the aluminum substrate and a subsequently deposited metal coating. When a part is immersed in the activator solution for an excessive period of time, a non-adherent smut forms which results in poor adhesion and appearance of a subsequently deposited metal coating.

Should there be smut formation due to excessive treatment time, where the smut formation is not excessive, the part may be reconditioned by treatment with a conventional desmutter such as a mixture of one part by volume hydrofluoric acid with three parts nitric acid at a temperature of from 75 to 85°F for a period of time sufficient to remove the loose or excessive smut and insufficient to remove any adherent conversion coating that may be present beneath the smut. Following treatment with the desmutter, the part should exhibit a clean, normally white to dark grey appearance with no areas of visible shiny metal.

The overall procedure for finishing aluminum in accordance with this invention requires a minimum of steps. If excessively soiled with grease, oil, crayon marks or the like, it is degreased or otherwise cleaned using standard procedures such as immersion in an etch type cleaner such as 5N caustic soda. The caustic undercuts and removes soil leaving an etched surface covered with a heavy, non-adherent smut which should be removed by immersion in a desmutter such as nitric or nitric-hydrofluoric mixtures. The part is then cold water rinsed and a uniform, adherent conversion coating is formed using procedures defined above, preferably with bath agitation. If a non-adherent smut forms over the conversion coating, it may be removed with a desmutter taking precautions to remove the aluminum part from the desmutter before it attacks the conversion coating, thereby exposing aluminum substrate. The part is rinsed and may be finished or it may be dried and stored or transported prior to finishing without formation of a damaging oxide film. Metal plating of the aluminum part is accomplished using standard procedures such as electroless or electrolytic metal plating.

The aluminum alloys within the scope of the invention are those containing at least 0.1 per cent, and preferably 0.5 per cent silicon as one alloying ingredient. Other alloying metals such as copper, iron, etc. may be present and do not interfere with the formation of the conversion coating.

Though not wishing to be bound by theory, it is believed that the presence of silicon in the alloy is responsible for formation of a conversion coating resistant to oxidation and receptive to metal deposition. The dissolution

of aluminum from the surface of the alloy leaves a layer enriched in silicon, possibly in the form of a silicon-aluminum intermetallic compound, along with other alloying metals insoluble in the treatment solution. This theory is substantiated by three factors. First, it is known in the art that silicon-aluminum intermetallic compounds are oxidation resistant. Secondly, it has been found that the process is inoperable in the presence of the fluoride ion. It is known in the art that fluoride ions attack and dissolve silicon whereas the attack of the other halide ions on silicon is minimal. Thirdly, it has been found that the process of the invention is only operable with aluminum alloys containing at least 0.1 per cent silicon.

The remainder of the disclosure will be directed to examples illustrating specific embodiments of the invention, but should not be construed as limiting the invention thereto.

In the examples, all metal plating was conducted using either electroless or electrolytic nickel. It should be understood, however, that any of the known electroless or electrolytic formulations that do not etch aluminum are suitable for plating over aluminum prepared for finishing in accordance with this invention.

The electroless procedure chosen for the purposes of illustration involved immersion of

the aluminum part in an electroless nickel bath of the following composition:

nickel sulfate	40 grams	
citric acid	30 grams	
sodium hypophosphite	40 grams	35
acetic acid	10 ml	
ammonium hydroxide	to pH 4.8	
distilled water	to total volume of 1 liter	

Bath temperature is maintained at about 200 degrees F. The aluminum part is immersed in the nickel bath for a total of two hours to form a nickel coating having a thickness of approximately 1 mil.

Electrolytic plating is performed by immersing the aluminum part in a conventional nickel electrolytic bath known as a "Watts Nickel-Plating Electrolytic Bath." The bath used in the examples is maintained at a pH of between 4.0 to 5.0 and operated at a temperature of about 130°F. Current density is maintained at 40 asf for a period of time sufficient to deposit a coating of approximately one mil thickness.

Reported compositions of aluminum alloys used in the Examples are set forth in the following table:

Alloy	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Other
Electrolytic									0.01
1100	0.50 <sup>(1)</sup>	0.50 <sup>(1)</sup>	0.20	0.05			0.10		0.15
3003	0.60	0.70	0.20	1.20			0.10		0.15
2024	0.50	0.50	4.0 <sup>(1)</sup>	0.60 <sup>(1)</sup>	1.10 <sup>(1)</sup>	0.10	0.25		0.15
5052	0.20 <sup>(1)</sup>	0.25 <sup>(1)</sup>	0.10	0.10	2.60 <sup>(1)</sup>	0.25 <sup>(1)</sup>	0.10		0.15
6061	0.60 <sup>(1)</sup>	0.70	0.30 <sup>(1)</sup>	0.10	1.00 <sup>(1)</sup>	0.30 <sup>(1)</sup>	0.25	0.15	0.15
7075	0.50	0.70	1.80 <sup>(1)</sup>	0.30	2.80 <sup>(1)</sup>	0.30 <sup>(1)</sup>	6.00 <sup>(1)</sup>	0.20	0.15
380	12.00	3.80							

<sup>(1)</sup> Approximate

A plated surface may be evaluated by any of three procedures. First, the part is inspected visually for blisters and voids. Second, the sample is heated at 300°C for one half hour followed immediately by quenching in cold water and inspection for blister formation. The third method, called the bend test, involves breaking a sample by folding it back and forth upon itself and inspecting the break for peeling of the metal coating from the aluminum substrate.

#### EXAMPLE 1

Test bars of a No. 1100 aluminum alloy measuring 3" x 1" x 1/32" were prepared and degreased in trichloroethylene vapor. Each bar was then immersed in a 3.5N hydrochloric acid solution maintained between 75°F and 80°F for a period of time varying between 1/2 and 15 minutes, removed, rinsed, inspected visually, metal plated with nickel using electroless procedures, and evaluated. It was found that uniform, adherent, very light grey

coatings were formed on bars immersed in solution for periods of time ranging between 4 and 7-12 minutes. Nickel coatings on these bars possessed excellent appearance, were free of blisters and voids following quenching, and did not peel from the substrate upon breaking of the bar.

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Test bars pretreated for a period of less than 4 minutes either possessed a non-uniform conversion coating with shiny aluminum streaks appearing on the surface of the test bars or retained a residual oxide coating. Nickel coatings deposited on these bars blistered or failed to adhere to the aluminum substrate. With treatment times in excess of 7-1/2 minutes, the conversion coatings formed were non-adherent and the nickel coatings deposited thereon were rough, blistered and peeled from the aluminum substrate.

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#### EXAMPLE 2

Repetition of the procedure of Example 1 substituting electrolytic nickel for electroless nickel yields comparable results, though the time to form an initial, complete deposit was substantially increased.

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#### EXAMPLE 3

The procedure of Example 1 was repeated with time of treatment maintained constant at 6 minutes and normality of the hydrochloric acid solution ranging between 0.1 and 12.0. It was found that light grey, adherent, conversion coatings were formed on bars immersed in hydrochloric acid solutions having a normality ranging between about 3.0 and 5.0. A nickel coating deposited on these test bars were adherent, did not peel and did not show blistering when quenched. Nickel coatings deposited on test bars treated with hydrochloric acid solutions having a normality below 3.0 or above 5.0 were blistered or non-adherent.

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#### EXAMPLE 4

The procedure of Example 1 was repeated with a hydrochloric acid solution maintained at 90°F, all other conditions remaining the same. The treatment time required to obtain optimum results varied between 3-1/2 and 5-1/2 minutes.

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#### EXAMPLE 5

A test bar of a No. 1100 aluminum alloy was prepared according to the procedure of Example 1. It was immersed in a 3.5N hydrochloric acid solution at room temperature for a period of 5 minutes, rinsed and dried. It was then allowed to stand in air for a period in excess of 48 hours and then plated using an electroless nickel solution. The nickel coating was found to have excellent appearance, was free of blisters and voids following quenching and did not peel from the aluminum substrate upon breaking of the test bar.

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#### EXAMPLE 6

The procedure of Example 5 was repeated, but the surface of the test bar following treatment in hydrochloric acid solution and exposure to the atmosphere for a period of time in excess of 48 hours was subjected to electron beam microanalyses as follows:

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A beam of electrons is accelerated with a high potential and focused by means of an electromagnetic lens to a diameter of about 1 micron at the surface of the specimen. The specimen acts as a primary source of X-rays. A continuous or white spectrum is produced as well as fluorescent X-rays characteristic of the elements excited by the electron beam. A chemical analysis of the excited areas is afforded by analysis of the characteristic X-ray line by means of a single crystal X-ray spectrometer. Two curved mica crystal focusing spectrometers employing flow-proportional counters were set up to record the characteristic X-ray spectrum in the 0.5 to 10 Å wavelength range (U through Mg.). In addition, one of the mica crystals was lead stearate coated to extend the analytical capability through boron.

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A portion of each surface was scraped in order to expose the substrate. The sample was then inserted into the microanalyzer.

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With the spectrometer aligned to record wavelengths characteristic of chlorine, the electron beam was positioned on the treated surface and exposed substrate with the available X-ray intensities being recorded. Chlorine was not detectable within the detectability limit of about 0.05w/o.

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The spectrometer was then aligned to record wavelength characteristics for oxygen. Analysis failed to detect a layer of oxide film on the surface of the aluminum.

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#### EXAMPLE 7

The procedure of Example 6 was repeated with a test bar prepared from a No. 6061 aluminum alloy. The results obtained are illustrated in Fig. 1 of the drawings wherein curve A is a representation of a spectral pattern for the aluminum substrate scraped clean of the conversion coating; curve B is a representation of the spectral analysis of the conversion coating; and curve C is a representation of the spectral analysis of the conversion coating, in powder form, scraped from the test bar.

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The curves indicate that the conversion coating is richer in alloying elements than the aluminum substrate and a comparison of curve A with curve C for silicon indicates that there is a substantial increase in the quantity of silicon in the conversion coating.

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#### EXAMPLE 8

The procedure of Example 6 was repeated with the substitution of a 3.0N solution of hydrobromic acid for hydrochloric acid. Spec-

tral analysis failed to detect the presence of oxygen in the conversion coating while showing a substantial increase in silicon content.

#### EXAMPLE 9

- 5 Test bars of various aluminum alloys were prepared following the procedure of Example 1 and were immersed in 3.5N hydrochloric acid solution. Plating was accomplished using  
10 an electroless nickel solution. The alloys treated and the treatment times are set forth in the following tables:

	Alloy	Pretreatment Time (min.) at 80°F
15	3003	2.5
	2024	4.5
	5052	9.0
	6061	2.5
	7075	3.5
20	380	4.5

All nickel coatings were smooth, did not blister when quenched and did not peel from the aluminum substrate.

#### EXAMPLE 10

- 25 Repetition of Example 9 with the substitution of an electrolytic aluminum having less than 0.01 per cent impurities failed to produce a conversion coating. An oxide film formed on  
30 treatment with hydrochloric acid and an electroless nickel coating failed to bond to the aluminum substrate.

#### EXAMPLE 11

- 35 Substitution of a 3.5N hydrobromic acid or hydriodic acid solution for hydrochloric acid in Example 9 yields comparable results, though time to form an acceptable conversion coating is slightly increased.

#### EXAMPLE 12

- 40 A solution was prepared having the following composition:

potassium iodide	50 gms.
sulfuric acid	50 mls
water	to 1 liter

methyl carbitol  
glycolmonoethyl ether  
methoxyacetaldehyde  
ethyl alcohol  
formamide  
acetone

A test bar of a No. 1100 aluminum alloy was prepared according to the procedure of Example 1 and immersed in the above solution maintained at 200°F for 15 minutes. An adherent, uniform, very white coating formed. An electroless deposit of nickel formed that was blister free, would not peel and possessed excellent surface appearance.

#### EXAMPLE 13

The procedure of Example 12 may be repeated with substitution of any of the following salts for potassium iodide with comparable results, though treatment time and/or bath temperature may require modification:

potassium chloride	magnesium chloride
potassium bromide	calcium chloride
sodium iodide	calcium bromide
sodium bromide	calcium iodide
magnesium iodide	cesium chloride
ammonium chloride	

#### EXAMPLE 14

The procedures of Examples 12 and 13 may be repeated with any of the following aluminum alloys with comparable results through pretreatment time and/or bath temperature may require modification:

No. 3003	No. 6061
No. 2024	No. 7075
No. 5052	No. 380

#### EXAMPLE 15

A solution was prepared by mixing 300 mls of concentrated hydrochloric acid with 700 mls of butyl carbitol. A No. 1100 alloy was prepared in accordance with the procedure of Example 1 and immersed in solution maintained at 150°F for 7 minutes. A uniform, adherent conversion coating formed. The test bar was rinsed in water, dried and allowed to stand in air for 48 hours. It was then nickel coated using an electrolytic nickel solution. The coating was free of blisters following breaking of the test bar.

#### EXAMPLE 16

The procedure of Example 15 may be repeated, with minor changes in conditions and substitution of the following materials for butyl carbitol:

butyl alcohol  
diethyleneglycolmonomethyl ether  
diethyleneglycolethyl ether  
dimethylformamide  
butyl cellosolve

## EXAMPLE 17

Three test bars of a No. 3003 aluminum alloy were prepared. Each was immersed in a 3.5N hydrochloric acid solution maintained at 80°F. for 10 minutes. A non-adherent, grey coating formed on the surfaces of the test bars. One test bar was immediately plated with electroless nickel. The coating was rough and peeled from the aluminum substrate. The second bar was immersed in a solution of three parts nitric acid and 1 part hydrofluoric acid at 80°F for 1 minute and rinsed in cold water. The bar had a clean white surface. The bar was plated with electroless nickel with formation of a smooth coating that did not peel from the aluminum substrate. The third bar was immersed in the same solution of nitric and hydrofluoric acid for 3 minutes. All of the non-adherent smut as well as the conversion coating was removed. An electroless nickel deposit did not adhere to the aluminum substrate.

## EXAMPLE 18

A solution was prepared by dissolving 50 grams of ferric chloride in one liter of water. A No. 1100 alloy prepared in accordance with Example 1 was immersed in the solution maintained at 80°F for 5 minutes to form a uniform, adherent conversion coating on the alloy. Deposition of electroless nickel resulted in a coating that did not peel from a broken bar and did not blister when quenched from 300°F.

## EXAMPLE 19

The procedure of Example 18 was repeated with ferric chloride solution containing from 50 to 500 grams per liter of ferric chloride. All solutions produced acceptable conversion coatings, though time for forming the coating decreased with increasing concentration of ferric chloride.

## EXAMPLE 20

A solution having a pH of about 7.0 was prepared from 50 grams of ammonium persulphate, 20 grams of sodium chloride and 1 liter of water. Immersion of a No. 1100 aluminum alloy in the solution maintained at 120°F for 5 minutes produced an acceptable conversion coating. An electroless nickel deposit applied over the conversion coating was smooth, adherent and blister free.

## EXAMPLE 21

Material	Concentration	
HCl (37%)	100 ml	55
Thiourea	5 gm	
H <sub>2</sub> SO <sub>4</sub>	100 ml	
butyl cellosolve	750 ml	
H <sub>2</sub> O	50 ml	

Test bars measuring 3" × 1" × 1/32" were prepared from the alloy of Table II and treated as follows:

	Step	Temperature	Time
	A. Vapor degrease in trichloroethylene		
	B. Immerse in 5% NaOH cleaner	160—180°F	15—45 seconds
	C. Cold water rinse	room	1—2 minutes
	D. Immerse in nitric acid deoxidizer	room	1—2 minutes
	E. Cold water rinse	room	1—2 minutes
	F. Immerse in above activator solution	98—102°F	(1)
	G. Cold water rinse	room	1—2 minutes
	H. Immerse in desmutter of 3 parts nitric acid, and 1 parts of hydrofluoric acid, if necessary, to remove non-adherent smut	75—85°F	15—90 seconds
	I. Cold water rinse	room	1—2 minutes
	J. Immerse in electroless nickel solution	200°F	2 hours
	K. Cold water rinse	room	30—90 seconds
	L. Dry		

(1) For a time as indicated in Fig. 2 of the drawings.

With reference to FIG. 2 of the drawings, the shaded portions represent treatment time where adherent, blister free nickel coatings were obtained that had good surface appearance and did not blister nor peel from the aluminum substrate with quenching and breaking of the sample. In the cross-hatched portion of the drawing, where short treatments were used, the aluminum substrate possessed a non-uniform conversion coating exhibiting a streaky appearance or retained a residual oxide coating. Nickel deposited over these test bars either blistered or failed to adhere to the aluminum substrate. In the cross-hatched portion of the drawing representing long treatment times, a coating deposited over the aluminum substrate was rough, blistered and easily peeled. A conversion coating did not form on the electrolytic sample.

In the above example, steps A through E are recommended for best results. However, unless the aluminum part is excessively soiled, these steps may be omitted. The step of desmutting (H) is required if a non-adherent smut forms on the surface of the aluminum

part. However, it must be carefully controlled to avoid removal of the conversion coating by excessive treatment.

#### EXAMPLE 22

Example 21 was repeated omitting steps A to E, H and I. Substantially similar results were obtained except that with some alloys, the time range to form an acceptable conversion coating was narrowed. This was due to increased time required to remove dirt and decreased maximum time due to omissions of the step of smut removal.

#### EXAMPLE 23

Repetition of the procedure of Example 21 substituting electrolytic nickel for electroless nickel yields comparable results, though the time to form an initial, complete nickel deposit is substantially increased.

#### EXAMPLE 24

Repetition of the procedure of Example 21 with treatment temperature of step F increased to 150°F results in a decreased time



### EXAMPLES 28—29

One No. 1100 aluminum alloy was immersed in nitric acid solution for 5 minutes, a second in sulfuric acid. A brown coating formed. Electroless nickel deposited directly over these coatings were non-adherent.

### EXAMPLE 30

A No. 1100 aluminum alloy was immersed in an aqueous 25% sodium chloride solution for 5 minutes. A white coating formed. Electroless nickel deposited directly over this coating was non-adherent.

20 EXAMPLE 27  
A No. 1100 aluminum alloy was immersed

The remaining examples are directed to compositions within the scope of the invention for formation of conversion coatings, but are not to be construed as limiting the invention thereto.

### EXAMPLES 31 TO 40

### Concentration

[illegible]

### Concentration

[illegible]

## EXAMPLES 51 TO 60

Example No.	Concentration									
	51	52	53	54	55	56	57	58	59	60
Material										
HCl (37%) ml	250									
HBr (46%) ml		200								
HI (48%) ml			200							
NaCl gm				100	200	250			200	
KBr gm							150	250		200
H <sub>2</sub> SO <sub>4</sub> (50%) ml									100	
H <sub>3</sub> PO <sub>4</sub> (48%) ml										100
formaldehyde (10%) ml		20								
thiourea gm	10									
resorcinol gm			25							
hydroquinone gm								25		
ferric chloride 1/2° Be ml						100				
ammonium persulphate gm	50			100			150			
potassium permanganate		50			100				100	
ceric ammonium nitrate gm			100					200		100
formamide ml	500									
butyl cellosolve ml		500	500				300			
water	to 1 liter of solution									

- The process of the invention provides numerous advantages over prior art procedures for metal plating over aluminum including the following:
1. Improved adhesion between deposited metal and substrate. Adhesion between a metal deposit and the aluminum substrate is not degraded upon exposure to elevated temperatures, and in some cases, adhesion is improved. By comparison, upon exposure to elevated temperatures for extended periods of time, adhesion is lost between a metal deposited using the zincate process and an aluminum substrate due to the diffusion of zinc into aluminum.
  2. Ease of process and low cost of materials. Zincating requires from 12 to 21 process steps using expensive and dangerous materials. The present invention requires no more than 12 procedural steps and frequently less. The process uses readily available inexpensive reagents.
  3. Oxidation resistance of the conversion coating permitting storage and/or transportation prior to metal coating without formation of oxygen films that would prevent adhesion

between aluminum substrate and a metal coating.

4. Ability to basket or barrel plate small aluminum parts. This is not possible with zincating because the coating cannot be disturbed until plated. The use of the process of the present invention eliminates racking of small parts.

While the invention has been described with respect to certain specific embodiments, it should be understood that it is susceptible to modification within the scope of the appended claims. For example, in the examples, all plating was conducted using either electroless or electrolytic nickel solutions. The plating step is not critical and the specific procedures used to plate and the plating compositions are not a part of the invention. Any metal heretofore used to plate over aluminum may be used to plate over aluminum pretreated in accordance with this invention. These metals include, for example, iron and mild steels, tin, brass, copper, silver, stainless steel, gold, etc. Typical electroless and electrolytic solutions for plating over aluminum are known in the art and described in many publications including Edwards et al, *The Aluminum Industry*, McGraw Hill Book Company, Inc., New York, 1930, pp. 492 to 499; Wernick et al, *Finishing of Aluminum*, Robert Draper Ltd., Teddington, England, 1959, Chapters 12 and 15; *Metal Finishing Guidebook*, Metals and Plastics Publications, Inc., Westwood, New Jersey, 1967, pp. 228 to 371; all included herein by reference.

#### WHAT WE CLAIM IS:—

1. A process for metal plating an aluminium alloy containing at least 0.1% silicon which comprises treating the surface of said alloy with an aqueous activator solution containing halogen ions other than fluoride ions and one or both of hydrogen ions and an oxidising agent, for a time in excess of that required to remove any oxide coating on the surface of said alloy and sufficient to selectively remove aluminium from the oxide free-surface of said alloy and thereby form an adherent conversion coating on the surface of said alloy which is enriched in silicon, and metal plating said alloy over said conversion coating.

2. A process according to claim 1 in which the solvent phase of the activator solution comprises a mixture of water and a water-miscible organic solvent.

3. A process according to claim 1 in which said activator solution contains an organic inhibitor effective to retard the rate of aluminium dissolution.

4. A process according to any one of the preceding claims in which the activator solution is formulated so that the treatment time necessary to form said conversion coating is at least 15 seconds.

5. A process according to claim 4 in which

said treatment time is at least 2 minutes.

6. A process according to any one of the preceding claims in which the activator solution is employed at a temperature below 120°F.

7. A process according to any one of the preceding claims in which said conversion coating is characterised in that substantially no oxide film is formed on its surface when tested by exposure to air under normal ambient conditions for 24 hours.

8. A process according to any one of the preceding claims in which the activator solution comprises 0.1 to 6 moles per litre of halide ion and 1 to 75 grams. per litre of organic inhibitor.

9. A process according to claim 8 in which the activator solution comprises 1 to 4 moles per litre of hydrogen ion.

10. A process according to claim 8 or claim 9 in which the activator solution comprises 0.3 to 1.5 moles per litre of oxidising agent.

11. A process according to any one of the preceding claims in which the halide ion is derived from hydrochloric acid, hydrobromic acid, hydriodic acid and metal salts of these acids where the metal cation does not deposit on an aluminium substrate.

12. A process according to any one of the preceding claims in which the oxidising agent comprises ferric ions, a permanganate, ceric, peroxide or chromate compound.

13. A process according to any one of the preceding claims in which the organic inhibitor is formaldehyde, urea, thiourea, methyl butynol, chlorendic acid, pentachlorophenol, resorcinol, catechol or hydroquinone.

14. A process according to any one of the preceding claims in which the solvent is a mixture of water with formamide, an alcohol, a glycol, or an ether of ethylene glycol.

15. A process according to any one of the preceding claims in which an electroless metal coating is deposited over the conversion coating.

16. A process according to any one of claims 1 to 14 in which an electrolytic metal coating is deposited over the conversion coating from a non-etching electrolytic solution.

17. A process according to any one of the preceding claims in which said metal plating is a nickel or nickel alloy plating.

18. A process according to claim 1 substantially as described with reference to the Examples.

19. A process according to any one of the preceding claims in which non-adherent smut is also formed on the surface of said alloy in addition to said conversion coating, and said smut is removed prior to metal plating by immersion in a desmutter for a period of time sufficient to remove loose, non-adherent smut and insufficient to remove the adherent conversion coating.

20. A process according to claim 19 in

which the desmutter comprises nitric acid or a mixture of nitric acid and hydrofluoric acid.

21. A metal plated aluminium alloy whenever produced by the process claimed in any  
5 one of the preceding claims.

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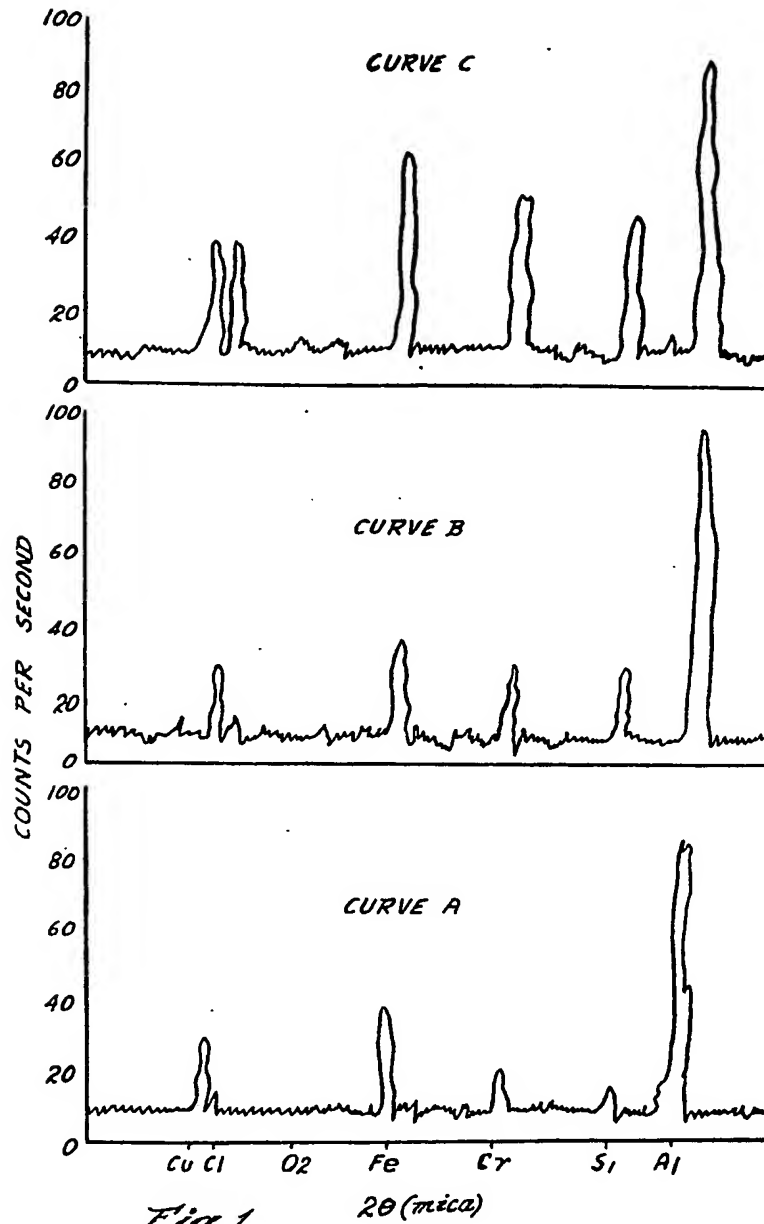
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## COMPLETE SPECIFICATION

2 SHEETS

This drawing is a reproduction of  
the Original on a reduced scale  
Sheet 1

*Fig. 1*

*TIME TO FORM CONVERSION COATING(MINUTES)*

ALLOY	2	3	4	5	6	7	8	9	10	11	12
1100											
2024											
3003											
5052											
6061											
7075											
6063											
356											
357											
380											
13X											
ELECTROLYTIC											

*Fig. 2*